From Titanium Oxydifluoride (TiOF₂) to Titania (TiO₂): Phase Transition and Non-metal Doping with Enhanced Photocatalytic Hydrogen (H₂) Evolution Properties

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Single-crystalline TiOF₂ crystals with cubical morphology were prepared via a facile solvothermal method and its transformation to anatase TiO₂ under different calcination conditions such as pure argon, moist argon and pure hydrogen sulphide (H₂S) was explored by using XRD/Raman/UV-Vis/SEM/TEM/SAED. The non-metal sulphur doping was successfully fulfilled and the doped TiO₂ microcubes showed the best photocatalytic H₂ evolution property.

Considering the conventional H₂ production, which has great reliance on depleting fossil fuels and suffers the carbon dioxide emission issue, direct splitting of water using a particulate semiconductor photocatalyst under sun light irradiation would be one of the most promising technologies to produce clean and recyclable hydrogen on a large scale in the future.¹⁻⁴ Developing high-efficient, stable photocatalysts or photocatalytic systems always plays an important role in water cleavage processes.⁵⁻⁹ Transition metal oxides with octahedrally coordinated d⁰ metal ions including Ti⁴⁺, Zr⁴⁺, Nb⁵⁺, and Ta⁵⁺ and some other metal oxides involving octahedrally coordinated d¹⁰ metal ions such as In³⁺, Sn⁴⁺, and Sb⁵⁺ have been reported as the candidates for water splitting.¹⁰ As the first generation photocatalyst for H₂ evolution, TiO₂-based semiconductor material has been widely studied, which also includes the endeavours to extend the adsorption spectrum to visible light region. Numerous efforts including crystal shape engineering, metal or non-metal doping and multi-component heterostructuring were made to enhance the photocatalytic efficiency.^{4,11-15} Recently, titanium oxydifluoride (TiOF₂) was proposed to be an active photocatalyst and its key role in the photo-degradation of 4-

Fig. 1 XRD patterns of the anatase TiO₂ prepared by heat-treating TiOF₂ at 600°C for 4 h in moist argon atmosphere (a), TiOF₂ crystals with anatase TiO₂ surface phase derived by heat-treating TiOF₂ at 300°C for 4 h in moist argon atmosphere (b), and original untreated TiOF₂ (c). d-f) Corresponding Raman spectra of the three samples shown in a-c).

chlorophenol under visible light irradiation was studied experimentally.¹⁶ However, pure TiOF₂ photocatalyst may have the issues such as low thermal stability, poor visible light adsorption, and non-ideal chemical resistance etc. Thus developing new photocatalysts derived from original TiOF₂ may overcome these disadvantages and the photocatalytic water cleavage efficiency might be also enhanced. Herein, we report a study on the transformation of TiOF₂ to anatase TiO₂ under different reaction conditions and sulphur doping on produced anatase TiO₂ was also fulfilled, which showed the enhanced optical and photocatalytic H₂ evolution properties.

Single-crystalline pure-phase TiOF₂ was synthesized *via* a simple solvothermal method using Titanium (IV) tetrafluoride (TiF₄) and 48% hydrofluoric acid (HF) solution as

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† Electronic Supplementary Information (ESI) available: Experimental details, TG and DSC spectra, XPS and SEM images of the transformation process under pure argon atmosphere.

Fig. 2 a-c) SEM/ Cross-sectional HRTEM images and SAED pattern of the as-obtained single-crystalline cubic TiOF₂ particles. d) and e) SEM images of TiOF₂ crystals with anatase TiO₂ surface phase and pure anatase TiO₂ prepared through calcinating the TiOF₂ crystals in moist argon atmosphere at 300°C and 600°C for 4 h, respectively. f) SEM image of anatase TiO₂ prepared through calcinating the TiOF₂ crystals in H₂S at 800°C for 4 h. g) and h) SEM images of anatase TiO₂ prepared through calcinating the TiOF₂ crystals in pure argon at 800°C for 4 h. i) TEM image and SAED pattern (the inset) of anatase TiO₂ prepared through calcinating the TiOF₂ crystals in pure argon at 800°C for 4 h.

the precursors, and n-butanol as the solvent (see Supporting Information for experimental details). **Caution!** *Hydrofluoric acid is extremely corrosive and it should be handled with extreme care.* The typical X-ray diffraction (XRD) patterns of the original untreated TiOF₂ (Fig. 1c) and the samples prepared by heat-treating original TiOF₂ crystals at 600°C and 300°C for 4 h in moist argon atmosphere (Fig. 1a and 1b) show the evolution of crystal phases. The overall bulk crystal phase was still kept as original cubic TiOF₂ (space group *Pm3m*, JCPDS No. 08-0060) when the sample was treated at 300°C for 4 h while phase pure anatase TiO₂ was generated if calcination temperature was increased to 600°C.¹⁶ Interestingly, Raman spectra of the sample prepared by heat-treating original TiOF₂ crystals at 300°C shows of typical tetragonal anatase TiO₂ phase instead of cubic TiOF₂ where strong bands at 147, 392, 519, 629 cm⁻¹ were observed (Fig. 1e). All of these bands can be assigned to the anatase phase with typical Raman bands at 144 (E_g), 399 (B_{1g}), 515 (A_{1g}), 519 (B_{1g}, superimposed with the 515 cm⁻¹ band), and 639 cm⁻¹ (E_g).¹⁷ This non-consistence between XRD and Raman spectra for the sample treated at 300°C is due to the *in situ* formation of anatase TiO₂ surface phase, which generally can only be detected by UV or visible Raman spectroscopy. Furthermore, consistent with the XRD result, the Raman spectra of the sample treated at 600°C (Fig. 1a and 1d) illustrates a typical anatase TiO₂ phase. Based on this structural information, it can be concluded that the phase transition from cubic TiOF₂ to tetragonal anatase TiO₂ should start from the surface of TiOF₂

microcubes and then extend to the whole particle. Moreover, thermal gravimetric (TG) and differential scanning calorimeter (DSC) analysis of the as-synthesized TiOF₂ were also carried out, indicating that the weight loss started to occur at 300°C and then the rate of weight loss increased significantly at 430°C (see Supporting Information Fig. S1). These results clearly illustrate a slow surface phase transition under low temperature and then a relative fast bulk phase transition under high temperature from TiOF₂ to anatase TiO₂. Furthermore, X-ray photoelectron spectroscopy (XPS) spectra (see Supporting Information Fig. S2) not only demonstrate the typically chemical compositions and bonding states of original TiOF₂ and anatase TiO₂ crystals but also give the evidence on the effective sulphur doping; the S 2p core electrons with its central position at 163.1 eV and 168.5 eV confirm the formation of sulphur doped anatase TiO₂.¹⁸⁻²⁴

Fig. 3 a-d) UV-vis spectra of original untreated TiOF₂ and the anatase TiO₂ prepared through calcinating the TiOF₂ crystals under moist argon, pure argon and H₂S, respectively.

Scanning electron microscopy (SEM), Cross-sectional high resolution transmission electron microscopy (HRTEM) images, and selected-area electron diffraction (SAED) pattern of the cubical TiOF₂ in Fig. 2a-c confirm the single crystalline characteristics and an inter-planar space of 0.38 nm between (100) planes. Due to the symmetries of the cubical TiOF₂ crystals, all the flat, square surfaces can be indexed into {100} facets. The single crystalline TiOF₂ cubes were then calcinated in moist argon, pure argon and pure H₂S at different temperatures (see Supporting Information for experimental details) and the corresponding SEM images are given in Fig. 2d-i. All the treated samples also exhibit a overall cubical shape and more interestingly, the internal hollow space was generate for the sample calcinated in pure argon (see Fig. 2g-i).²⁵ The XRD patterns (see Supporting Information in Fig. S3) further confirm the products shown in Fig. 2d-h are phase-pure anatase TiO₂ crystals. The scale-like nanosheets can also be observed on the external surface of anatase TiO₂ crystals (Fig. 2g-h), which might be exposed by high-reactive {001} facets due to the fluorine-rich TiOF₂ raw materials.⁵ More importantly, the external surface of all the generated anatase TiO₂ microcrystals should also be high-reactive (001) because of the existence of F capping agent and

small lattice mismatch ($\sim 0.34\%$) between the (100) plane of cubic TiOF_2 (space group $Pm\bar{3}m$, $a, b, c = 3.798 \text{ \AA}$)^{16,24} and the (001) plane of tetragonal anatase TiO_2 (space group $I4_1/amd$, $a, b = 3.7852 \text{ \AA}$ and $c = 9.5139 \text{ \AA}$).⁵ However, when TiOF_2 was treated at 900°C under the same pure argon atmosphere, the formed anatase TiO_2 crystals have a smooth surface without {001} faceted nanosheets (Fig. S4d) which might be due to the effective fluorine removal under high temperature. More SEM images of the products treated at different temperatures are given in Fig. S4. The optical properties of the original untreated TiOF_2 and the samples calcinated under moist argon, pure argon and H_2S were monitored by UV-vis spectroscopy and the results in Fig. 3 clearly indicate that the phase transition from TiOF_2 to anatase TiO_2 can increase the photon adsorption in the visible light region. Sulphur doping will further enhance the visible light response.²⁶

In order to study the photocatalytic properties of the original TiOF_2 and various derived anatase TiO_2 crystals, we then measured the efficiency of hydrogen evolution of all the samples loaded with 1 wt % Pt in the presence of methanol as a scavenger (see Supporting Information for the experimental details). As shown in Fig. 4, the sulphur doped anatase TiO_2 crystals have the highest photocatalytic efficiency ($7054.5 \mu\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$) and the original TiOF_2 did not demonstrate detectable photocatalytic activity for H_2 evolution, which matches well with the corresponding UV-vis spectra in Fig. 3.

Fig. 4 The photocatalytic water splitting properties of the as-obtained TiOF_2 (■) and the anatase TiO_2 crystals prepared through calcinating the TiOF_2 crystals under moist argon (●), pure argon (▲) and H_2S (▼), respectively.

In summary, using Titanium Oxydifluoride as solid precursor, phase transition and non-metal doping were fulfilled to generate various anatase TiO_2 crystals with enhanced photocatalytic H_2 evolution properties. Single-crystalline TiOF_2 with cubic morphology was prepared using a simple solvothermal method and its transformation to anatase TiO_2 crystals under different calcination atmosphere such as pure argon, moist argon and pure hydrogen sulphide (H_2S) were studied systematically, which reveals that treating conditions have impact on the overall morphology, optical property and photocatalytic activity of the final products.

Notes and references

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1. A. Fujishima, K. Honda, *Nature*, 1972, **238**, 37.
2. M. Yoshino, M. Kakihana, W. S. Cho, H. Kato, A. Kudo, *Chem. Mater.*, 2002, **14**, 3369.
3. J. Sato, N. Saito, H. Nishiyama, Y. Inoue, *J. Phys. Chem. B*, 2003, **107**, 7965.
4. G. Liu, H. G. Yang, X. W. Wang, L. N. Cheng, J. Pan, G. Q. Lu, H. M. Cheng, *J. Am. Chem. Soc.*, 2009, **131**, 12868.
5. H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng, G. Q. Lu, *Nature*, 2008, **453**, 638.
6. J. H. Park, S. Kim, A. J. Bard, *Nano Lett.*, 2006, **6**, 24.
7. J. Rossmeisl, K. Dimitrievski, P. Siegbahn, J. K. Nørskov, *J. Phys. Chem. C*, 2007, **111**, 18821.
8. S. Y. Ryu, W. Balcerski, T. K. Lee, M. R. Hoffmann, *J. Phys. Chem. C*, 2007, **111**, 18195.
9. M. Yoshida, A. Yamakata, K. Takanabe, J. Kubota, M. Osawa, K. Domen, *J. Am. Chem. Soc.*, 2009, **131**, 13218.
10. K. Ikarashi, J. Sato, H. Kobayashi, N. Saito, H. Nishiyama, Y. Inoue, *J. Phys. Chem. B*, 2002, **106**, 9048.
11. S. C. Li, L. N. Chu, X. Q. Gong, U. Diebold, *Science*, 2010, **328**, 882.
12. H. G. Yang, H. C. Zeng, *J. Phys. Chem. B*, 2004, **108**, 3492.
13. S. W. Liu, J. G. Yu, M. Jaroniec, *J. Am. Chem. Soc.*, 2010, **132**, 11914.
14. J. Yu, Q. Xiang, J. Ran, S. Mann, *CrystEngComm*, 2010, **12**, 872.
15. J. Yu, L. Qi, M. Jaroniec, *J. Phys. Chem. C*, 2010, **114**, 13118.
16. J. Zhu, D. Zhang, Z. Bian, G. Li, Y. Huo, Y. Lu, H. Li, *Chem. Commun.*, 2009, **453**, 5394.
17. T. Ohsaka, *J. Phys. Soc. Jpn.*, 1980, **48**, 1661.
18. X. W. Lou, H. C. Zeng, *J. Am. Chem. Soc.*, 2003, **125**, 2697.
19. G. Liu, C. Sun, S. C. Smith, L. Wang, G. Q. Lu, H. M. Cheng, *J. Colloid Interface Sci.*, 2010, **349**, 477.
20. E. L. D. Hebenstreit, W. Hebenstreit, U. Diebold, *Surf. Sci.*, 2001, **470**, 347.
21. T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, *Appl. Phys. Lett.*, 2002, **81**, 454.
22. F. Saito, Q. Zhang, J. Kano, *J. Mater. Sci.*, 2004, **39**, 5051.
23. W. Ho, J. C. Yu, S. Lee, *J. Solid State Chem.*, 2006, **179**, 1171.
24. X. Tang, D. Li, *J. Phys. Chem. C*, 2008, **112**, 5405.
25. J. C. Lytle, H. Yan, R. T. Turgeon, A. Stein, *Chem. Mater.*, 2004, **16**, 3829.
26. G. Liu, L. Wang, H. G. Yang, H. M. Cheng, G. Q. Lu, *J. Mater. Chem.*, 2010, **20**, 831.